Actual and potential mobilisation of Zn, Cd and Pb from floodplain sediments in mining regions: an example from the Geul

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INTRODUCTION

During the last decades, large-scale investigations of the spatial distribution of heavy metals in floodplain sediments contaminated by mining and smelting activities have been performed at many different locations in Europe. Particular attention is mostly paid to the use of overbank sediments as a tool to reconstruct de pollution history of a river catchment. For this purpose, 'total' metal concentrations are usually determined in the alluvial sediments. However, very few studies focus on the speciation, mobility and toxicity of heavy metals in alluvial sediments in mining regions. Sometimes an attempt is made to relate the results of sequential extractions and the mineralogical analysis of metal-bearing phases to the potential mobility of heavy metals. However, sequential extractions only result in an operationally defined fractionation of metals, which is difficult to link to real environmental conditions. The present study focuses on the *actual* and *potential* risk of the contamination of alluvial sediments in mining regions. To estimate the actual risk of the contamination, $CaCl_2$-extractions were performed and plant uptake of heavy metals was investigated. The potential mobility of Zn, Cd and Pb was assessed with pH_{stat} leaching tests and EDTA-extractions.

METHODOLOGY

Five vertical profiles were sampled in detail within overbank sediments along the Geul river in Plombières (East-Belgium) and in Sippenaeken and Epen (northern part of the Netherlands), respectively 1, 3 and 6 km downstream from the mine tailing of Plombières and respectively 7, 9 and 12 km downstream from the mine tailing of La Calamine. Total metal concentrations, pH, grainsize, CEC and organic carbon content were determined for all the samples.

Single extractions with $CaCl_2$ (0.01 M) and EDTA (0.05 M) were performed to estimate the 'actual' (i.e. porewater composition) and 'potential' mobilisation of Cd, Zn and Pb from the overbank sediments. Furthermore, heavy metal uptake by stringing nettle (*Urtica dioica L.*) was determined by analysing total Zn-, Cd- and Pb-concentrations in the shoot, leaf, root and flower of the plant. Finally, the acid neutralizing capacity and potential mobilisation of trace metals was investigated with pH_{stat} leaching tests (e.g. Cappuyns et al., 2004).

RESULTS AND DISCUSSION

Overbank sediments along the Geul river are mainly contaminated with Zn (279-13171 mg/kg), Pb (38-6350 mg/kg) and Cd (0.1-37 mg/kg) (minimum and maximum of 100 samples) and pH is between 5.4 and 8.0. Total Zn-, Pb- and Cd-concentrations in overbank sediments decrease with increasing distance from the mine tailings and display a low acid neutralizing capacity (ANC) and CEC, resulting in a relatively low retention of heavy metals. The 'mobile' fraction of Cd and Zn (as determined with a $CaCl_2$ extraction) can be predicted by EDTA-extractable Cd- and Zn-concentrations, pH and organic carbon content ($r=0.87$-0.95, $\alpha=0.05$).

$CaCl_2$-extractable Zn- and Cd-concentrations also decrease with increasing distance from the mine tailings. This decrease in 'mobile' Zn- and Cd-concentrations is reflected in lower

Zn- and Cd-concentrations in stringing nettle further away from the mine tailings (Table 1). The highest Zn-concentrations are found in the leaves, whereas Cd is more evenly distributed among the different plant parts. For Pb, significant different concentrations are measured in roots and aboveground plant parts (Table 1).

Table 1: Zn-, Cd- and Pb-concentrations in the the $CaCl_2$ extract and in different parts of stinging nettle. Values in mg/kg.

	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
	Plombières			Sippenaeken			Epen		
$CaCl_2$	162	0.78	0.58	81	0.48	0.21	33	0.17	0.22
root	833	0.99	17	450	1.71	28	70	0.08	8
shoot	2885	1.03	1	668	0.57	3	177	0.13	2
leaf	3282	0.61	3	1928	0.34	2	335	0.04	3
flower	1355	0.81	6	473	0.32	2	219	0.14	4

Although the acid neutralizing capacity (ANC) decreases from Plombières to Epen (Fig. 1), pH_{stat} leaching tests (pH 4) indicate a lower release of Zn, Pb and Cd upon acidification (Fig. 1). This suggests a stronger incorporation of Zn, Pb and Cd in overbank sediments more downstream from the mine tailing. Despite the lower ANC in the downstream part of the alluvial plain, acidification yields a lower risk than in the overbank sediments located more upstream.

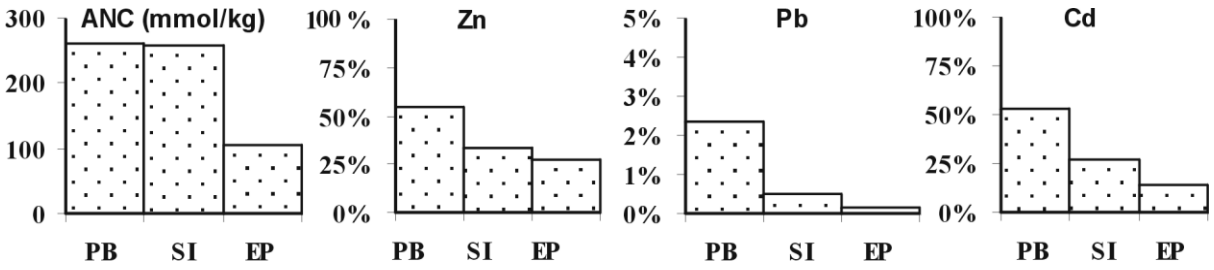

Fig.1: ANC and release of Zn, Pb and Cd during pH_{stat} leaching at pH 4 in Plombières (PB), Sippenaeken (SI) and Epen (EP). Release of Zn, Pb and Cd is expressed as % of total concentration

CONCLUSION

'Mobile' Zn- and Cd-concentrations (as determined with a $CaCl_2$ 0.01M extraction) in the alluvial plain of the Geul could be related to the 'available' Zn- and Cd-content and soil properties and to Zn- and Cd-uptake by stringing nettle. Additionally, pH_{stat} leaching tests provided more information concerning acid neutralizing capacity and potential mobilisation of trace metals and therefore they are considered to be a better alternative to sequential extractions, which are usually applied to study 'heavy metal fractionation' in mining regions.

REFERENCES

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